TiNi基合金の低温における構造相転移と超弾性

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論文内容要約

Chapter 1: Introduction

Ti-Ni shape memory alloys (SMA) are widely used for industrial and medical applications due to their good shape memory properties, mechanical properties and corrosion resistance. The addition of a third element into Ti-Ni binary alloy has been used to change the martensitic transformation temperatures. For example, in the Ti-Ni-Pd and Ti-Ni-Hf systems, substitutions of Pd and Hf for Ni and Ti, respectively, make the martensitic transformation temperatures increase [1]. On the other hand, although low-temperature SMAs are expected to be also useful for applications in cryogenic equipment, there are only few studies on the low-temperature SMAs, in comparison with those on the high-temperature SMAs [2, 3].

Since reported by Hwang *et al.* in $Ti_{50}Ni_{47}Fe_3$ alloy in 1983 [4], the Commensurate-Incommensurate (C-IC) transition has continuously received attention as a precursor state before R-phase transition, in relation to the $1/3\{110\}_{B2}$ diffuse scattering, where the IC-state is characterized by the diffuse scattering reflections appearing at off-set positions near the $1/3\{110\}_{B2}$. In the cooling process, the reflections shift to the precise 1/3 position and finally lock-on in the C-state. While many researchers have examined the $1/3\{110\}_{B2}$ diffuse scattering and nanoscale microstructure manly in TiNiFe alloy [5], the origin and influence to martensitic transformations are still under discussion. Moreover, the details of the martensitic transformation and the C-IC transition in the Ti-poor portion of Ti-Ni based alloys, where the transformation temperature decreases, are also unknown.

In the thesis, in order to reveal them, the effects of C-IC transition on martensitic transformation temperature, entropy change and superelastisity (SE) are systematically investigated for the Ti-poor portion in Ti-Ni, Ti-Ni-Cu and Ti-Ni-Fe alloys.

The doctor thesis is composed of six chapters.

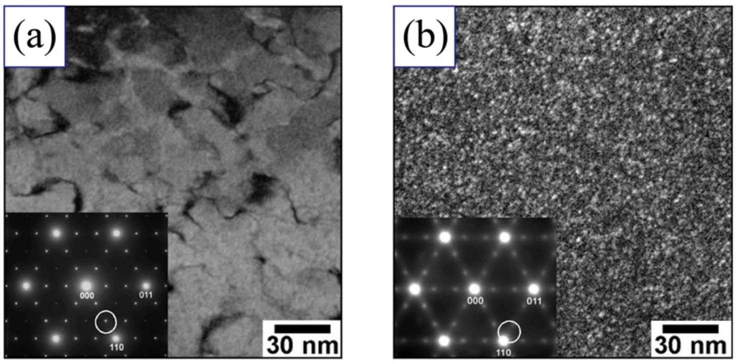

Fig. 1 The dark-field images in $Ti_{50.0}Ni_{48.0}Fe_{2.0}$ alloy. (a) R-phase at T=296.0 K, (b) C-state (I-phase) at T=248.0 K. [5]

Chapter 2: Structural Phase Transition at Low Temperatures in Ti-Ni Based Alloys

In this chapter, dependence of Ni content on martensitic transformation behavior is investigated for Ti-Ni based alloys, i.e., $Ti_{50.0-x}Ni_{50.0+x}$, $Ti_{50.0-x}Ni_{40.0+x}Cu_{10.0}$ and $Ti_{50.0-x}Ni_{47.0+x}Fe_{3.0}$ alloys.

It is revealed that the C/IC transition influences the martensitic transformation in Ti-Ni based alloys. By thermoanalysis with high-resolution DSC measurement, it is confirmed that martensitic transformation temperatures decrease with increasing Ni content in Ti-Ni based alloys. Furthermore, the broad peaks were observed in Ni-rich region, as shown in C_P-T curves of Fig. 2. In this research, the reaction accompanying broad peak is termed "Intermediate (I)"-phase transformation. The broad peak in the present research seems to correspond to the C-IC transition previously reported [5]. (The details on the in-situ TEM observation are reported in chapter 3) The I-phase transformation temperatures (T_A) are almost independent of the Ni content. As shown in Fig.3, martensitic transformation temperature decreases with increasing Ni content more drastically in the I-phase region. This means that the stability of martensite phase decreases due to existence of the I-phase.

The transformation entropy change (ΔS) during phase transformations decreases with increasing Ni content. The total transformation entropy change in I-phase region, $\Delta S^{\mathrm{Total}}$ can be given by the sum of ΔS^{I} and ΔS^{i} (i=B19-phase, R-phase) and the $\Delta S^{\mathrm{Total}}$ was found to be continuous against the Ni content in the I-phase region.

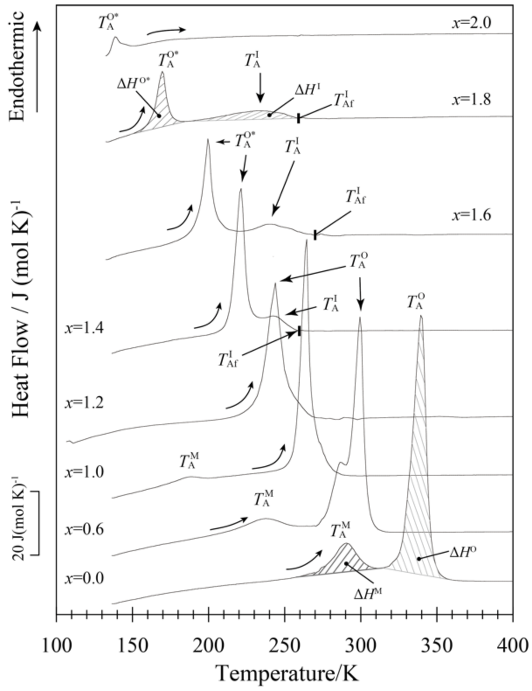

Fig. 2 C_P-T curves in $Ti_{50.0-x}Ni_{40.0+x}Cu_{10.0}$ alloys

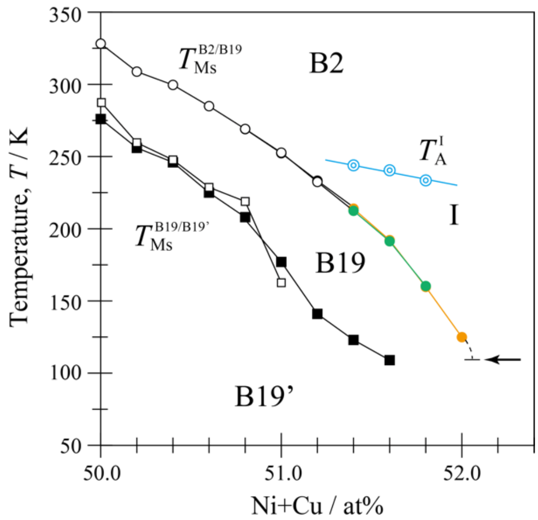

Fig. 3 Ni contents dependence on transformation temperatures in $Ti_{50.0-x}Ni_{40.0+x}Cu_{10.0}$ alloys

Chapter 3: Microstructure of Intermediate (I) Phase in Ti-Ni Based Alloys

In this chapter, in-situ TEM observation is carried out for Ti-Ni-Cu and Ti-Ni-Fe alloys to examine the influence of I phase to nanoscale microstructures in the Ti-Ni based alloys.

For $Ti_{48.2}Ni_{41.8}Cu_{10.0}$ alloys, the diffuse scattering reflection appearing at off-set positions near the 1/3{110} $_{B2}$ reflections were observed at 183K. The reflections shift to the precise 1/3 position and finally lock-on in the C (I)-phase, as shown in Fig. 4. For $Ti_{50.0-x}Ni_{47.0+x}Fe_{3.0}$ alloy, the ordinary twin boundary microstructure of R-phase was confirmed at T=87K. On the other hands, for off-stoichiometric $Ti_{49.6}Ni_{47.4}Fe_{3.0}$ alloy, the fine domain structure was formed even in the R-phase region at T=87K. This result means that in the case of R-phase via I-phase transformation, the microstructure of R-phase is significantly influenced by existence of the I-phase.

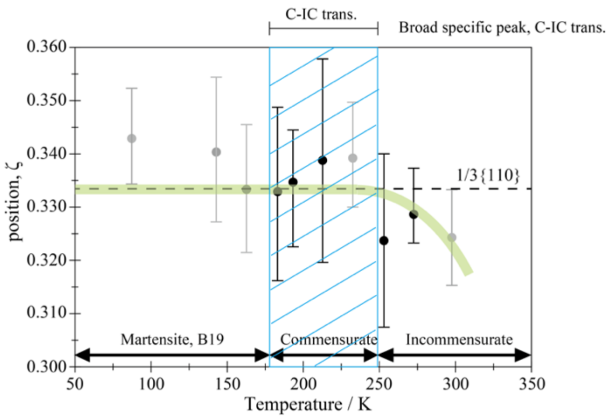

Fig. 4 Temperature dependence on peak position, {ζζ0} in $Ti_{48.2}Ni_{41.8}Cu_{10.0}$ alloys

By all the microscopic observations with in-situ TEM observation, the I-phase is concluded to correspond to the C-state in the C-IC transition of the Ti-Ni based alloys.

Chapter 4: Superelastisic Behavior at Low Temperatures in Ti-Ni Based Polycrystalline Alloys

In this chapter, in order to compare the temperature dependence on stress hysteresis (σ_{hys}) between the binary TiNi and the ternary TiNiCu alloys, superelastic behavior at low temperatures in $Ti_{47.6}Ni_{42.4}Cu_{10.0}$ polycrystalline alloy is investigated.

The temperatures dependence on stress hysteresis, σ_{hys}, could be well fitted using $\sigma_{hys}(T)/2 = \sigma_\mu + \sigma_{TA}(0)\{1-(T/T_{TA})^{1/q}\}^{1/p}$, where $\sigma_{TA}(0)$ and σ_μ are the thermal activation and the athermal terms, respectively, and T_{TA} is the critical temperature at which the thermal activation term disappears. p and q are fitting parameters related to the shape of energy barrier against migration of habit plains.

The stress-induced transformation (SIT) takes place at 50K and the critical stresses of forward and reverse SIT, σ_{Ms} and σ_{Af}, were clearly detected at temperatures above 60 K. The half of stress hysteresis, $1/2\sigma_{hys}$ ($=1/2(\sigma_{Ms}-\sigma_{Af})$) drastically increases with decreasing temperature below T_{TA}=163K. The temperature dependence itself of the stress hysteresis in $Ti_{47.6}Ni_{42.4}Cu_{10.0}$ alloy is very similar to that in $Ti_{48.2}Ni_{51.8}$ alloy [3]. The combination of p and q is the same as that of $Ti_{48.2}Ni_{51.8}$ alloy, and the value of σ_μ was found to show no significant difference from that of the binary alloy [3]. However, T_{TA} and σ_{TA} (0) are apparently lower than those of binary alloy [3]. Thus,

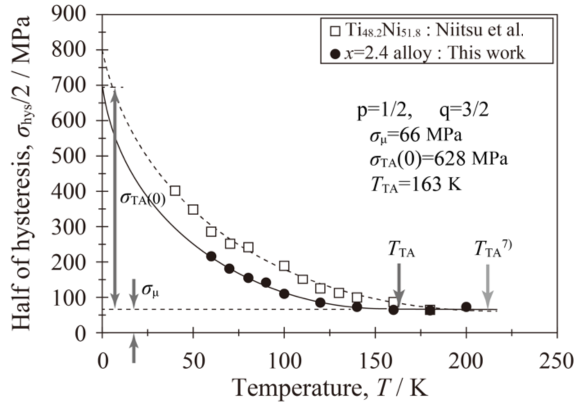

Fig. 5 Temperature dependence on stress hysteresis in $Ti_{47.6}Ni_{42.4}Cu_{10.0}$ alloys

the σ_{hys} of $Ti_{47.6}Ni_{42.4}Cu_{10.0}$ alloy is lower than that of $Ti_{48.2}Ni_{51.8}$ alloy at the same temperature in the whole temperature range below about 160 K.

Chapter 5: Superelastic Behavior at Low Temperatures in Ti-Ni Single Crystal Alloy

In this chapter, to more deeply examine the influence of I phase to mechanical properties in Ti-Ni alloy, the single crystal samples of Ti-Ni binary alloy were prepared to evaluate the superelastic properties.

The stress hysteresis (σ_{hys}) drastically increases with decreasing temperature in low temperature region also in single crystal alloy annealed at 1003K for 12h. The behavior of the σ_{hys} is very similar to that in Ti-Ni polycrystalline alloy [3]. Therefore, the increase of σ_{hys} at low temperatures may universally occur, regardless of single-crystalline or polycrystalline condition.

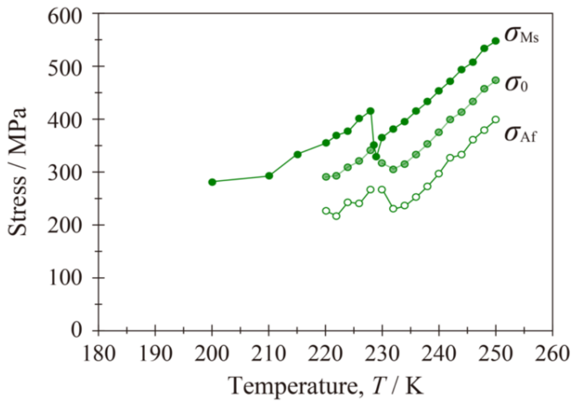

Fig. 6 Temperature dependence on σ_{Ms}, σ_{Af} and σ_0 for <110>$_{B2}$ case in 973K12h aged Ti-Ni single crystal

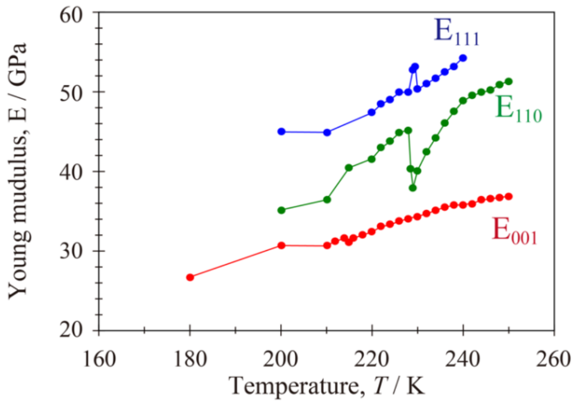

Fig. 7 Temperature dependence on young modulus in 973K12h aged Ti-Ni single crystal

In compression test along <110>$_{B2}$ for single crystal annealed at 973K for 12h, the σ_{Ms} and σ_{Af} show discontinuity near T=230K as exhibited in Fig. 6 and Young modulus, E_{110}, shows an abnormal behavior in the same temperature range as shown in Fig. 7. Together with the result of specific heat measurement for the same sample, it is strongly suggested that this anomaly is caused by the I-phase transformation. The further investigation is needed to clarify the origin of the abnormal phenomena of σ_{Ms}, σ_{Af} and E_{110} in Ti-Ni single crystal alloy.

Chapter 6: Conclusions

In this chapter, the contents of chapters 1 through 5 are summarized.

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